

Synthesis and Epoxy Curing of Mannich Bases Derived from Bisphenol A and Poly(oxyalkylene)diamine

JIANG-JEN LIN,¹ SHIAU-FENG LIN,¹ TSO-TING KUO,¹ FENG-CHIH CHANG,² FENG-PO TSENG²

¹ Department of Chemical Engineering, National Chung-Hsing University, Taichung, Taiwan

² Institute of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan

Received 19 August 1999; accepted 18 February 2000

ABSTRACT: A family of Mannich bases were prepared from the reaction of 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A or BPA), formaldehyde, and poly(oxyalkylene)diamines at 1 : 1 : 1 or 1 : 2 : 2 molar ratio. By varying the molar ratio of bisphenol A to amine and the chemical structures of poly(oxyalkylene)diamines, a series of products with multiple functionalities of primary/secondary amines, phenols, and poly(oxyalkylene) were prepared. The curing profiles of these products toward the diglycidyl ether of bisphenol A (DGEBA) were examined by a differential scanning calorimeter (DSC). The physical properties of these cured materials were correlated with the chemical structures of the Mannich bases. Compared with the poly(oxyalkylene)diamines, the built-in phenol moiety in Mannich bases accelerated the curing rate. Both amine and phenol functionalities could be reactive sites toward diglycidyl ethers in a step-wise fashion under catalytic (triphenylphosphine) and different temperature conditions. Furthermore, the cured polymers demonstrated improved properties including tensile and flexural strength in comparison with those cured by the corresponding poly(oxyalkylene)diamines. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 615–623, 2000

Key words: Mannich base; poly(oxyalkylene)diamine; bisphenol A; epoxy resin

INTRODUCTION

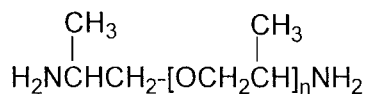
Epoxy polymers have been extensively exploited because of their superior properties and wide applications.^{1–3} Among the epoxy curing agents, the Mannich bases have been popularly used due to the structural versatility. The condensation of phenols, formaldehyde, and amines, namely the Mannich reaction, was first reported in 1942.^{4,5} The reaction is very versatile for industrial applications.^{6,7} It is known that the phenol-containing

compounds, such as poly(*p*-vinylphenol) or 2,3,6-tris(dimethylamino methyl)phenol, can accelerate epoxy/amine curing processes.^{8,9} The rate of nucleophilic ring opening of epoxides by amine curing agents can be enhanced in the presence of phenol compounds.^{1,10,11} Another advantage of using Mannich bases is to convert low molecular weight (M_w) poly(oxyalkylene)diamine curing agents into prepolymers that can improve the physical properties of cured materials. Low M_w poly(oxyalkylene)diamines such as triethyleneglycoldiamine usually generate the products of high hydrophilicity and brittleness due to the high crosslinking density. Their modified analogs including carboxylic acid-derived amidoamines and phenol-derived Mannich bases could overcome these drawbacks.^{11,12}

Correspondence to: J.-J. Lin.

Contract grant sponsor: The National Science Council of Taiwan.

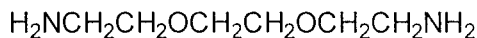
Journal of Applied Polymer Science, Vol. 78, 615–623 (2000)
© 2000 John Wiley & Sons, Inc.



n=2-3 (Jeffamine[®] D-230)

n=5-6 (Jeffamine[®] D-400)

poly(propylene glycol) bis(2-aminopropyl ether)



triethyleneglycoldiamine (Jeffamine[®] EDR-148)

Figure 1 Chemical structures of starting poly(oxyalkylene)diamines.

Recently, we have explored the Mannich bases prepared from simple phenols and dicyclopentadiene (DCPD).¹³ The flexibility of the cured epoxies was enhanced by the introduction of the tricyclodecane moieties. In this article, we report the preparation of the Mannich bases from bisphenol A and poly(oxyalkylene)diamines. The products are composed of various functionalities including phenols, primary/secondary amines, and poly(oxyalkylene) segments at different compositions. The methodology of preparing these bisphenol A-derived Mannich bases allows us to tailor a family of desired prepolymers as epoxy curing agents because BPA can provide four reactive sites for the variation. The curing process towards DGEBA was characterized by using a differential scanning calorimeter (DSC), and the mechanical properties of cured materials were tested. The relationship between the physical properties and the chemical structures is purposely addressed.

EXPERIMENTAL

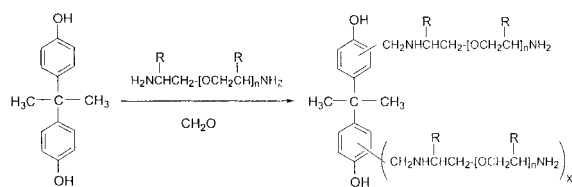
Materials

The poly(oxyalkylene)diamines including poly(propylene glycol) bis(2-aminopropyl ether) at an average M_w of 230 (i.e., Jeffamine[®] D-230), and 400 (i.e., Jeffamine[®] D-400), and triethyleneglycoldiamine at an M_w of 148 (i.e., Jeffamine[®] EDR-148) were obtained from Huntsman Chemical Company. Their chemical structures are shown in Figure 1. Liquid epoxy resin, diglycidyl ether of

bisphenol A (DGEBA) with an epoxide equivalent weight of 188 (trade name BE-188) was purchased from Nan-Ya Chemicals of Taiwan, and 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A or BPA) from Showa Chemical Company, and formalin from the TEDIA Company.

Preparation of Mannich Bases

The typical experimental procedures for preparing Mannich bases are described: to a 1-L four-necked round-bottom flask, equipped with a mechanical stirrer, a thermometer, a heating mantle, and a Dean-Stark trap, were added bisphenol A (228.0 g, 1.0 mol), poly(propylene glycol) bis(2-aminopropyl ether) at an average M_w of 230 (230.0 g, 1.0 mol) and toluene (100 mL). The mixture was heated to 50°C while stirring, until it reached homogeneity. The mixture was allowed to cool down to an ambient temperature and was followed by adding formalin (81.0 g, 1.0 mol) dropwisely through a dropping funnel. After completing the formalin addition, the reactor was heated to 80–90°C for 3 h and was further increased to 100–110°C. At this temperature, the generated water was removed slowly through a Dean-Stark trap. Finally, the temperature was raised to 120–130°C for an additional 2 h. The reactor was then cooled to 90°C, and subjected to low vacuum pressure to reduce water and toluene solvent. The recovered product was a sticky, yellow liquid (adduct **1a**). Using a similar procedure but different starting materials and stoichiometric ratios such as bisphenol A/CH₂O/diamine = 1/1/1 or 1/2/2, adducts involving three different poly(oxypropylene)- and poly(oxyethylene)-diamines were



	x = 0		x = 1		
	n	R	n	R	
1a	2-3	CH ₃	1b	2-3	CH ₃
2a	5-6	CH ₃	2b	5-6	CH ₃
3a	2	H	3b	2	H

Figure 2 The representative structures of Mannich bases prepared from various poly(oxyalkylene)diamines.

prepared. Six theoretical structures with mono- and di-substituted BPA Mannich compounds ($x = 0$ and $x = 1$, respectively) are illustrated in Figure 2.

Epoxy Curing in DSC

Equivalent amounts of adducts **1a**, **2a**, **2b**, **3a**, or **3b** and epoxy resin BE-188 (DGEBA with average epoxide equivalent weight of 188) were mixed at an ambient temperature and agitated until homogeneity. The homogenized mixture was quickly placed in a differential scanning calorimeter (DSC) instrument to measure its maximum exothermic temperature (T_p) and the glass transition temperature (T_g). Triphenylphosphine (Ph_3P) as an accelerator (2 wt % based on epoxy) was added to the curing mixture in some cases.

In a set of control experiments, a series of physical mixtures of starting materials were used as curing agents. As an example, the stoichiometric amounts of bisphenol A and BE-188 were mixed at 100°C until becoming homogeneous. The mixture was allowed to cool, and the calculated amount of the starting diamine was then added at either ambient temperature or lower. The prepared samples were quickly placed in DSC for the measurement. In the specific case of highly reactive diamine such as triethyleneglycoldiamine, the samples were prepared near the freezing point to minimize the reaction before measurement.

Preparation of Specimens for Mechanical Tests

The mixtures of the prepared Mannich bases and epoxy resin BE-188 were physically agitated and degassed at 50°C in a vacuum oven for about 5 min. The mixtures were then poured immediately into a preheated steel mold with caves. These caves were dogbone shaped for tensile tests and rectangular of different size for flexural or Izod impact tests. When the phenoxyl groups (—OH) were considered as reactive sites in addition to amines (—NH) in the calculation of equivalent weight towards epoxide, triphenylphosphine (Ph_3P) was added as catalyst (2 wt % based on epoxy). The curing temperature cycle was 50°C 1 h, 100°C 2 h, and 150°C 2 h. In the case of poly(propylene glycol) bis(2-aminopropyl ether) of 230 M_w (Jeffamine® D-230), the mixing and degassing process were carried out at room temperature. The resin mixture was cured under a sim-

ilar heating cycle to that described above. The mixture of triethyleneglycoldiamine (Jeffamine® EDR-148) and epoxy had partly cured during agitation and before degassing. The bubbles remaining in the mixtures occasionally induced failure in preparing the test specimens.

Instrumentation

The $^1\text{H-NMR}$ characterization was carried out by a Varian Unity Inova FT-NMR (600 MHz) spectrometer using CDCl_3 as solvent. FTIR spectra were obtained using a Perkin-Elmer Paragon 500 FTIR spectrometer. The measurements using a differential scanning calorimeter (DSC) were carried out on a Seiko DSC 5200 at a heating rate of 10°C/min under nitrogen. Gel permeation chromatography (GPC) analyses were performed in a HP 1090M HPLC using THF as the eluent, calibrated by polystyrene standards. Tensile properties were measured according to ASTM D638-86 at a testing rate of 5 mm/min, and flexural properties were measured according to ASTM D790 at a testing rate of 2.6 mm/min using an Instron machine. Notched Izod impact tests were carried out at ambient conditions according to the test method of ASTM D256. Amine contents were estimated by using the ASTM D2073-92 titration method.

RESULTS AND DISCUSSION

Syntheses of Mannich Bases

The Mannich reaction of bisphenol A, formaldehyde (CH_2O), and diamines including triethyleneglycoldiamine (EDR-148) and poly(propylene glycol) bis(2-aminopropyl ether) of 230 (D-230) and 400 M_w (D-400) produced a series of Mannich bases, according to the reaction described in Figure 2. The bisphenol A molecule has four reactive sites towards formaldehyde addition, providing many possibilities for the structural variation in this reaction. By varying the starting diamines and BPA, the products can be structurally diversified. The Mannich bases prepared from bisphenol A/ CH_2O /diamine = 1/1/1 (adduct **1a**, **2a**, **3a**) and 1/2/2 (adduct **1b**, **2b**, **3b**) are listed in Table I. Attempts to prepare the products of bisphenol A/ CH_2O /diamine = 1/3/3 failed, due to the formation of unworkable crosslinked gel materials. The analyses of amine contents in the prepared prod-

Table I The Mannich Products of Bisphenol A, Formaldehyde, and Poly(oxyalkylene)diamines

Adduct	Amine Contents (mEq/g)		Molecular Weight Distribution	
	Calculated	Found	Calculated	GPC
1a	4.3	4.4	470	640
1b	5.6	5.8	712	893
2a	3.1	3.0	640	832
2b	3.8	4.3	1050	1500
3a	5.2	5.4	388	612
3b	7.3	7.7	548	770

ucts were generally in good agreement with the theoretical values, as shown in Table I. The GPC analyses revealed the distribution of the weight-averaged molecular weight (M_w) of these products and residual starting materials or byproducts (Fig. 3). The main peaks corresponded to the products of the calculated M_w based on the stoichiometric molar ratios in Table I. These products are considered to be the mixtures of analogous Mannich bases.

The typical IR spectrum of adduct **1a** indicates the characteristic absorption at $3200\text{--}3400\text{ cm}^{-1}$ (—NH stretch), $2800\text{--}3000\text{ cm}^{-1}$ (alkyl group), 1600 cm^{-1} and 1500 cm^{-1} (aromatic $\text{C}=\text{C}$ stretch), 1103 cm^{-1} (C—O stretch, vs), 1258 cm^{-1} (aliphatic C—N stretch). Two representative $^1\text{H-NMR}$ spectra of products **1a** and **1b** are given in Figures 4 and 5, respectively. The following chemical shifts are assigned: $\delta 0.95\text{--}1.2\text{ ppm}$ (O—C—C—CH_3), $\delta 1.5\text{--}1.6\text{ ppm}$ (Ph—C—CH_3), $\delta 3.0\text{--}3.7\text{ ppm}$ (—NH—NH_2 and OCH_2CH), $\delta 6.6\text{--}7.1\text{ ppm}$ (aromatic). The observed $\delta 3.7\text{--}4.0\text{ ppm}$ is the characteristic chemical shift for the methylene linkages ($\text{Ph—CH}_2\text{—N}$) in the Mannich structures.^{14,15} The ratio of area integration for peaks ($\text{Ph—CH}_2\text{—N/aromatic protons/Ph—C—CH}_3=0.07/0.11/0.09$) is in good agreement with the theoretical structure of adduct **1b** at 4/6/6. For adduct **1a** ($\text{Ph—CH}_2\text{—N/aromatic protons/Ph—C—CH}_3=0.05/0.18/0.14$) the integration ratio is also in agreement with 2/7/6 according to its structure. Similar IR and NMR spectrums were observed in other adducts (**1b–3b**).

In general, adducts of molar ratio 1/1/1 (**1a**, **2a**, **3a**) have apparently higher viscosity than the corresponding 1/2/2 (**1b**, **2b**, **3b**) analogs. This may be due to the presence of higher relative

content of the rigid bisphenol A moiety in the molecular structures of 1/1/1 adducts.

Epoxy Curing

The prepared Mannich bases were allowed to react with the epoxy BE-188 in DSC to determine the curing profiles. Mannich bases cured epoxy with different stoichiometric amount of amine (denoted as —NH stoichiometry in Table II) or amine + phenol (denoted as $\text{—NH} + \text{—OH}$ stoichiometry in Table II). The peaks of maximum exothermic temperature (T_p) and glass transition temperature (T_g) of the cured polymers are important indications for the nature of these curing agents. These features of curing behavior are summarized in Table II.

The differences in molecular weights of the Mannich bases affected the curing kinetics. For example, the adducts derived from D-230 exhibited a lower T_p than the D-400 analogs. Particu-

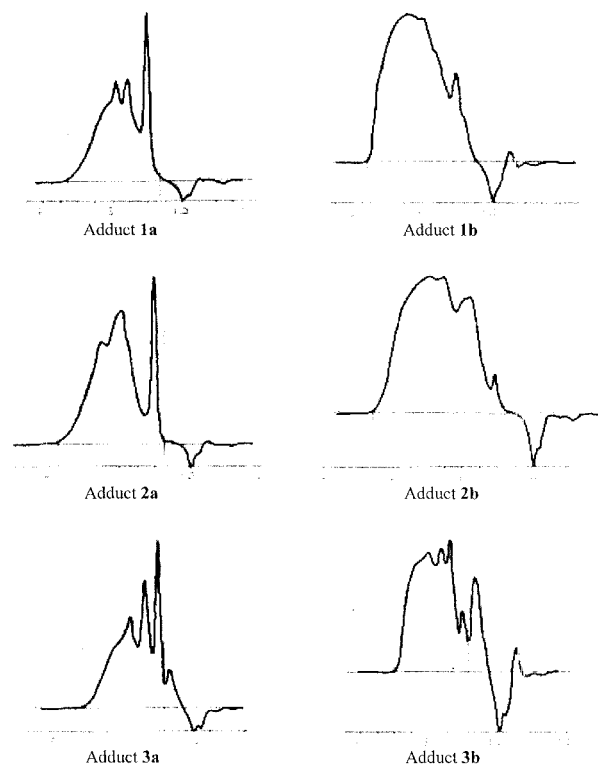


Figure 3 The M_w distribution of Mannich bases: adduct **1a** ($\text{BPA/CH}_2\text{O/D-230} = 1/1/1$); adduct **1b** ($\text{BPA/CH}_2\text{O/D-230} = 1/2/2$); adduct **2a** ($\text{BPA/CH}_2\text{O/D-400} = 1/1/1$); adduct **2b** ($\text{BPA/CH}_2\text{O/D-230} = 1/2/2$); adduct **3a** ($\text{BPA/CH}_2\text{O/EDR-148} = 1/1/1$); adduct **3b** ($\text{BPA/CH}_2\text{O/EDR-148} = 1/2/2$).

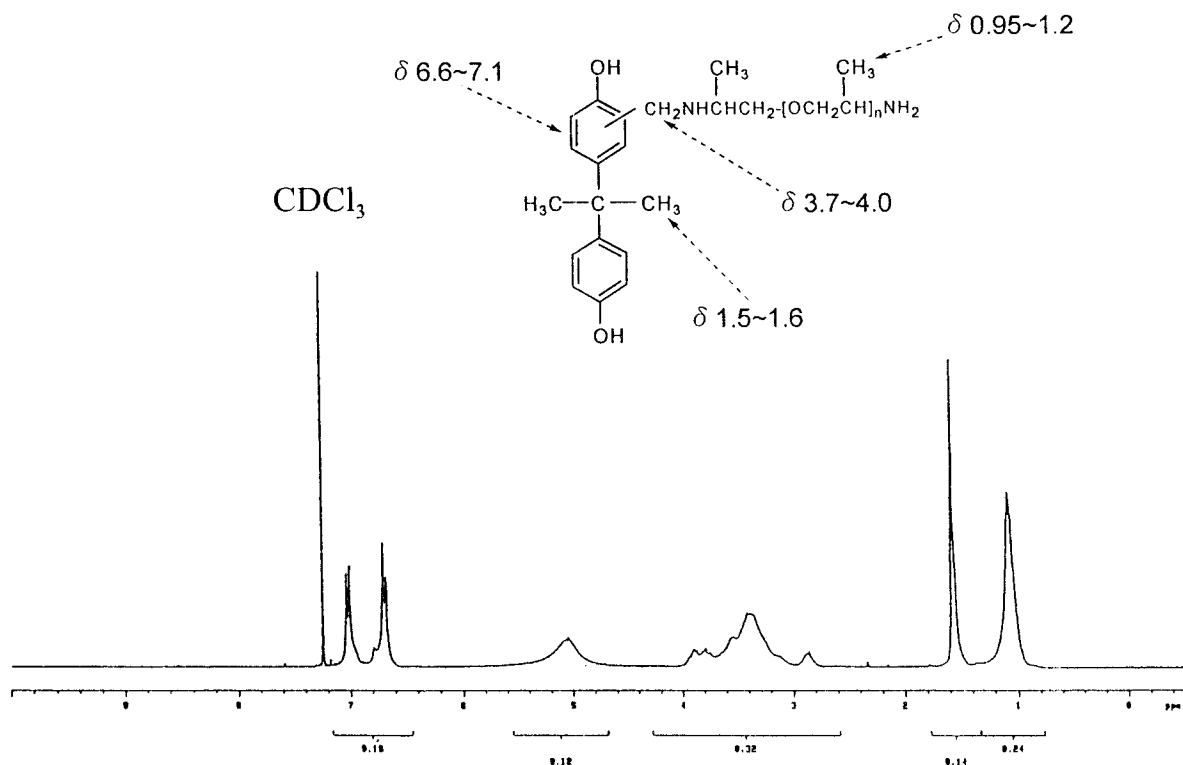


Figure 4 The ¹H-NMR spectra of adduct 1a.

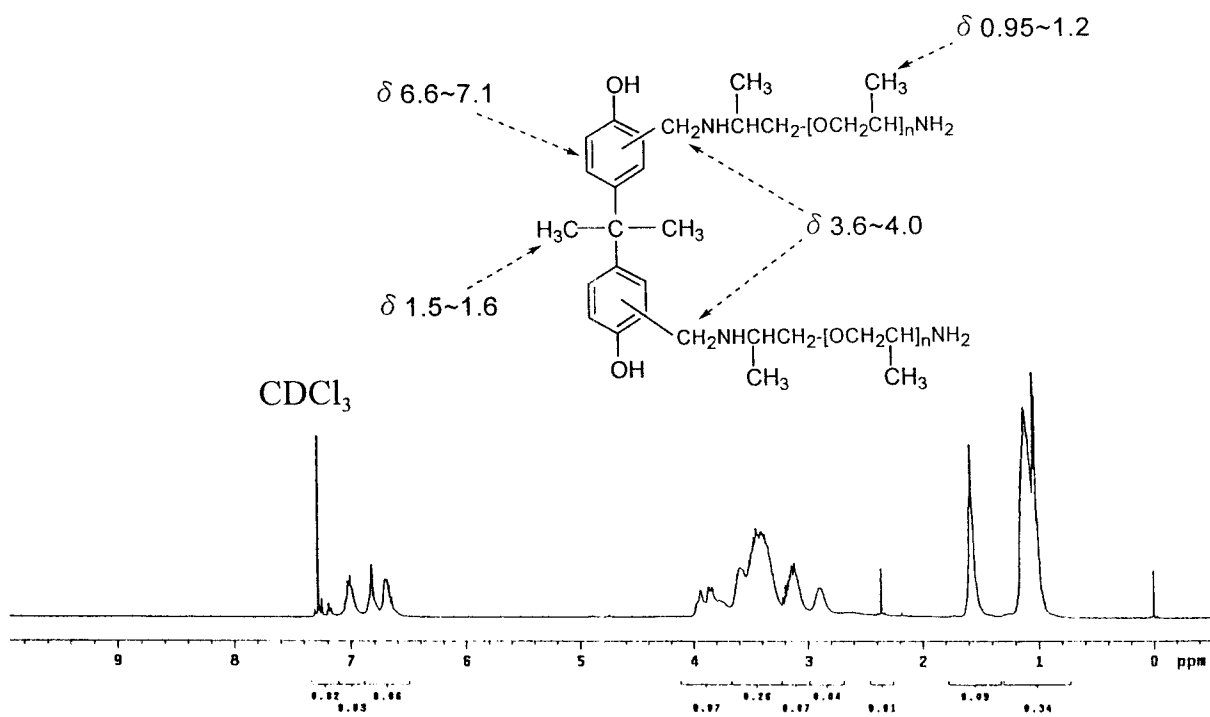


Figure 5 The ¹H-NMR spectra of adduct 1b.

Table II The Maximum Exothermic Temperature (T_p) and Glass Transition Temperature (T_g) of Epoxy Process in a Differential Scanning Calorimeter

Curing Agent	Stoichiometry	Bisphenol A wt %	T_p (°C)		T_g (°C)
D-230	—NH	0	130		77.6
D-400	—NH	0	139		42.7
EDR-148	—NH	0	105		92.7
1a	—NH	58.3	97	206	89.7
1b	—NH	53.1	113	218	80.1
2a	—NH	50.1	104	208	50.1
2b	—NH	44.9	120	223	48.4
3a	—NH	63.4	78	241	85.7
3b	—NH	58.4	91	242	82.3
1a	—NH + —OH	60.5	96	132	93.5
1b	—NH + —OH	55.4	112	220	92.1
2a	—NH + —OH	53.9	123	227	68.7
2b	—NH + —OH	48.1	130	231	61.2
3a	—NH + —OH	64.3	85	215	86.5
3b	—NH + —OH	59.8	93	233	85.3
Control experiment (physical mixture of BPA + diamine)					
1a'	—NH	18.8	90		81.7
1b'	—NH	12.6	98		66.6
2a'	—NH	16.5	95		50.3
2b'	—NH	10.6	105		37.9
3a'	—NH	24.3	74		60.6
3b'	—NH	13.8	83		36.2
1a'	—NH + —OH	12.3	94	138	92.2
1b'	—NH + —OH	10.4	104		76.0
2a'	—NH + —OH	13.0	97	135	60.6
2b'	—NH + —OH	9.0	106		49.5
3a'	—NH + —OH	17.3	82		93.8
3b'	—NH + —OH	11.2	87		79.9

larly, the mixtures of triethyleneglycoldiamine (EDR-148) based adducts and epoxy cured at very low temperatures. It appears that the curing temperature is related to the structure. The curing profiles of adducts **1a** and **1b**, prepared from D-230, with epoxy in stoichiometric amounts of amine (—NH) to epoxide were shown in Figure 6. The T_p s of the epoxy curing with adduct **1a** and **1b** are both lower than that of curing with the starting material D-230. This can be explained by the accelerating effect of the phenoxy groups (from bisphenol A) on the amine/epoxide reaction. The relative content of phenol moieties in adduct **1a** is higher than in adduct **1b** in leading to lower T_p in the curing profile. Similar results were also observed for paired adducts **2a/2b** and **3a/3b**. The polymers derived from adducts **1a** and **1b** have a higher T_g (89.7 and 80.1°C) than that from D-230 (77.6°C). This is attributed to the existence of rigid bisphenol A structures in adducts **1a** and

1b. The same trend was observed in adducts **2a** and **2b**. But for EDR-148, the extremely high crosslinking densities of cured polymer had a higher T_g (92.7°C) than those obtained from the corresponding Mannich bases (85.7°C for **3a** and 82.3°C for **3b**). Furthermore, epoxies cured from the Mannich bases of bisphenol A/amine=1/1 (**1a**, **2a**) generally showed higher T_g than the analogs at bisphenol A/amine 1/2 (**1b**, **2b**), due to the higher content of bisphenol A moieties.

The adducts **1a** and **1b** cured epoxy with stoichiometric amount of amine + phenol (—NH + —OH) were shown in Figure 7. The exotherms of more complicated patterns were observed, presumably due to the additional phenol curing with epoxide in the existence of catalyst. It was found that the T_g of cured polymers from —NH + —OH stoichiometry was higher than those from —NH stoichiometry. This imputes to the increase of the bisphenol A weight fraction in the network.

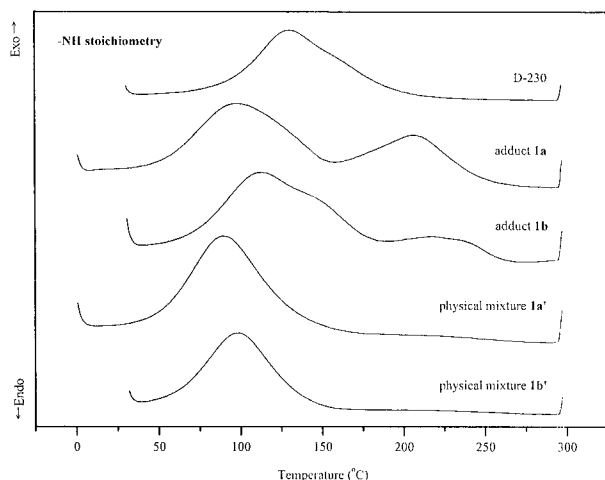


Figure 6 The curing profiles of D-230 derivatives with epoxy by stoichiometric amine in DSC.

Therefore, the phenoxy group contributes to the curing process not only as an accelerator but also as a crosslinking site for epoxies. In the control experiment, the physical mixtures (BPA + diamine) of control experiments had apparently low viscosity compared to the analogous Mannich bases. Used as curing agents, the physical mixtures showed lower T_p than the corresponding Mannich adducts, as demonstrated in Figures 6–7 as well as Table II. This phenomenon was observed repeatedly in different curing systems including D-230, D-400, and EDR-148. It can be explained by the better mobility for the physical

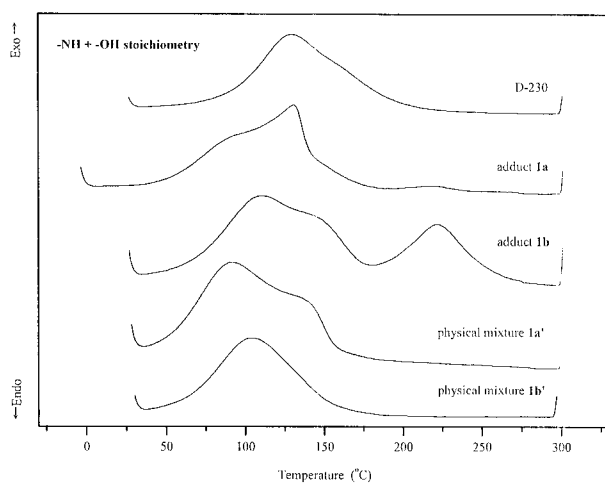


Figure 7 The curing profiles of D-230 derivatives with epoxy by stoichiometric amine plus phenol in DSC.

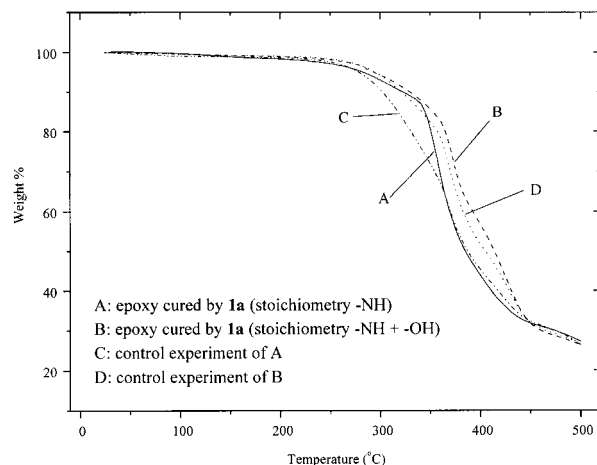


Figure 8 Thermal gravimetry analysis of epoxies cured by D-230 derivatives in air.

mixture as a curing agent during the curing process in relation to the Mannich bases. The physical mixtures cured polymers generally have lower T_g than those from Mannich bases.

The epoxy materials cured with the Mannich bases had a generally higher thermal stability than those cured with the corresponding physical mixtures. A higher crosslinking density caused by the use of the Mannich bases as curing agents is assumed. The thermal stability of several representative epoxies by TGA in air are shown in Figure 8.

Overall, the Mannich bases prepared from bisphenol A and poly(oxyalkylene)diamine had a generally higher curing reactivity than the corresponding poly(oxyalkylene)diamines. The curing rate was accelerated due to the presence of phenoxy group in the Mannich base. In all cases, the Mannich bases had more than one curing exotherm because of the structural complexity.

The nature of functionalities in chemical structures contributes differently to the physical prop-

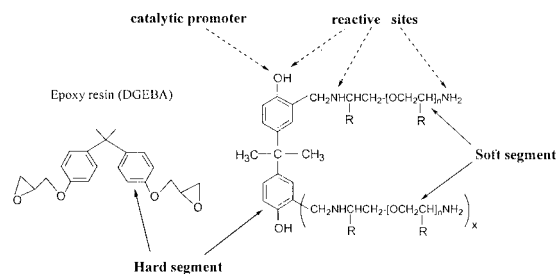


Figure 9 Structures and nature of Mannich bases and epoxy resin.

Table III The Mechanical Properties of Epoxies Cured by the Mannich Bases

Curing Agent	Equivalents	Tensile		Flexural	Izod
		Tensile Strength (MPa)	Strain at Break (%)	Flexural Strength (MPa)	Notch Izod Impact Strength (J/M)
D-230	—NH	60.4 (5.7)	10.3 (2.7)	108.1 (1.4)	59
1a	—NH + —OH	64.1 (2.5)	8.9 (0.4)	116.4 (1.2)	48
1b	—NH + —OH	77.8 (0.9)	13.8 (0.8)	120.2 (3.7)	50
D-400	—NH	51.9 (1.1)	7.9 (0.1)	81.4 (0.3)	47
2a	—NH	52.6 (10.5)	7.1 (2.2)	96.2 (4.7)	37
2b	—NH	54.2 (3.4)	9.9 (0.7)	87.4 (1.2)	56
2a	—NH + —OH	61.8 (1.1)	10.3 (0.9)	91.9 (0.8)	46
2b	—NH + —OH	59.3 (0.4)	10.8 (0.6)	93.1 (0.3)	53
		Control experiment (physical mixture of BPA + diamine)			
2a'	—NH	53.1 (4.0)	7.0 (0.9)	92.6 (2.5)	39
2b'	—NH	56.0 (1.1)	10.0 (0.3)	86.4 (0.1)	38
2a'	—NH + —OH	59.8 (0.5)	11.0 (0.9)	90.8 (1.8)	42
2b'	—NH + —OH	56.4 (0.9)	10.6 (0.6)	84.6 (0.1)	40

erties. The poly(oxyalkylene) segment is flexible in comparison with the bisphenol A backbone in nature (Fig. 9). The bisphenol A is a rigid structure, which also exists in the epoxy structure (DGEBA). It seems the relative contents of poly(oxyalkylene) vs. BPA determine the properties of the epoxy products.

Mechanical Properties

The factors contributing to the mechanical properties can be also explained by the structural versatility as shown in Figure 9. The hard and soft segments in the Mannich base structure generated different epoxy polymer networks. The comparison of mechanical properties between the poly(oxyalkylene)diamines and the Mannich bases is summarized in Table III. Compared to the starting material D-230 (or D-400), the Mannich base-cured materials exhibited an improvement in tensile strength and flexural modulus. This is credited to the bisphenol A in the Mannich base structure. Bisphenol A in the Mannich base structures had contributions as a hard segment and also good compatibility with epoxy. Similarly, the epoxies cured with —NH + —OH stoichiometry had higher tensile strength than those cured with —NH stoichiometry, due to the higher weight fraction of bisphenol A (Table II). With the incorporation of soft segments of poly(oxyalkylene)diamines, the D-400 derivatives are more flexible than those from D-230. Therefore, the

epoxies cured from D-400 derivatives exhibited lower tensile strength and lower T_g than those from D-230 derivatives. In the Izod impact strength, the Mannich bases at 1/2 molar ratio (adducts **1b**, **2b**) performed better than the analogs of 1/1 molar ratio (adducts **1a**, **2a**), similarly due to higher relative amount of poly(oxypropylene) structure in adducts **1b** and **2b**. When the physical mixtures were used as curing agents in control experiments, there were no significant changes in composition compared to the Mannich bases, and hence, no apparent changes on mechanical properties.

CONCLUSIONS

The Mannich reactions of bisphenol A, formaldehyde, and poly(oxyalkylene)diamines at 1 : 1 : 1 or 1 : 2 : 2 molar ratios afforded a series of Mannich bases. These products consisted of multiple functionalities of primary/secondary amines, phenols, and flexible poly(oxyalkylene) segments. Three types of reactive sites (primary amine, secondary amine, and phenol) in the Mannich base structure showed off in the complexity of curing profiles in DSC. Compared with the starting poly(oxyalkylene)diamines, the Mannich bases had a faster curing profile or cured at lower temperatures, due to the accelerating effect by the phenoxies. The tailored Mannich structures had a diversity of

functionalities, which has curing properties in a stepwise manner. Furthermore, the cured polymers from Mannich bases had improved mechanical properties. The curing profiles and the mechanical properties can be correlated with the Mannich structures.

The financial support from the National Science Council of Taiwan is acknowledged.

REFERENCES

1. May, C. A. *Epoxy Resin: Chemistry and Technology*; Marcel Dekker Inc.: New York, 1988.
2. Lee, H.; Neville, K. *Epoxy Resins*; McGraw-Hill: New York, 1959.
3. Lee, H.; Neville, K. *Handbook of Epoxy Resins*; McGraw-Hill: New York, 1982.
4. Blicke, F. F. *Organic Reactions*; J. Wiley & Sons: New York, 1942, p. 303, vol. 11.
5. Tramontini, M.; Angiolini, L. *Mannich Bases: Chemistry and Uses*; CRC Press: Boca Raton, FL, 1994.
6. Tramontini, M.; Angiolini, L.; Ghedini, N. *Polymer* 1988, 29, 771.
7. Leigh, D. A.; Linnae, P.; Jackson, G. *Tetrahedron Lett* 1993, 34, 5639.
8. Bagga, M. M.; Bull, C. H. U.S. Pat. 4, 659, 779, 1986.
9. Grigsby, R. A., Jr.; Speranza, G. P. U.S. Pat. 4, 714, 750, 1986.
10. Suzuki, H.; Matsui, A.; Inoue, T. U.S. Pat. 3, 950, 451, 1973.
11. Lin, J. J.; Speranza, G. P.; Waddill, H. G. *J Appl Polym Sci* 1997, 66, 2339.
12. Lin, J. J.; Speranza, G. P.; Waddill, H. G. *J Polym Res* 1996, 3, 97.
13. Tseng, F. P.; Chang, F. C.; Lin, S. F.; Lin, J. J. *J Appl Polym Sci* 1999, 71, 2129.
14. Jamois, D.; Tessier, M.; Marechal, E. *J Polym Sci Part A Polym Chem* 1993, 31, 1923.
15. Jamois, D.; Tessier, M.; Marechal, E. *J Polym Sci Part A Polym Chem* 1993, 31, 1959.